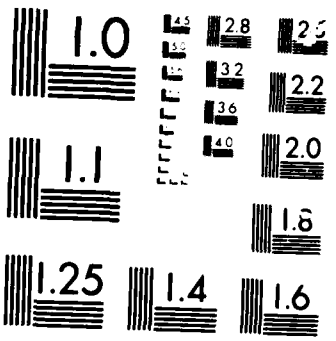
AD-A169 032 NUCLEAR REACTION ANALYSIS OF HYDROGEN IN METALS(U) 1/1
STATE UNIV OF NEW YORK AT ALBANY DEPT OF PHYSICS
W A LANFORD 23 MAR 86 ARO-18265.20-MS DAAG29-82-K-0036
UNCLASSIFIED F/G 7/5 NL



UNCLASSIFIED
RITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(2)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

EPORT NUMBER: ARO 18265.20-MS | 2. GOVT ACCESSION NO.: N/A | 3. RECIPIENT'S CATALOG NUMBER: N/A

ITLE (and Subtitle)

Nuclear Reaction Analysis of Hydrogen in Metals

5. TYPE OF REPORT & PERIOD COVERED: Final Jan. 82 - Sept. 85

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): DAAG29-82-K-0036

W.A. Lanford

8. CONTRACT OR GRANT NUMBER(s)

PERFORMING ORGANIZATION NAME AND ADDRESS
Physics Department
SUNY Albany
Albany, NY 12222

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE: March 23, 1986

13. NUMBER OF PAGES: 19

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrogen, Metals, Nuclear Reaction Analysis, Thin films

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research accomplishments of a contract to utilize nuclear reaction analysis to study hydrogen in materials are summarized. These include development of new techniques (high sensitivity, non-vacuum, Doppler spectroscopy, superlattice ...), the application of these techniques to study stress and electric current effects on hydrogen distribution in metals and the application of these methods to a variety of new materials.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

NUCLEAR REACTION ANALYSIS OF HYDROGEN IN METALS

FINAL REPORT

WILLIAM A. LANFORD

FEBRUARY 20, 1986

U.S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAG29-82-K-0036

DEPARTMENT OF PHYSICS
SUNY ALBANY
ALBANY, NEW YORK 12222

OVERVIEW OF RESEARCH ACCOMPLISHMENTS

Most of the work carried under this contract has been or is in the process of being published and has been previously reported to the Army Research Office. Hence, this report will consist principally of an outline of how these different published results fit together under the overall topic of the use of nuclear reaction analysis to study hydrogen in metals.

Immediately following this report is a numbered list of the papers which have been written under this contract. Below, we will refer to the various publications by their number in this list.

Briefly, the papers prepared under this contract can be grouped under four headings: (I) Development of new techniques for the study of hydrogen in materials, (II) Studies of how macroscopic variables (stress and electric currents) effect the distribution of hydrogen in metals, (III) Studies of the effects of hydrogen in various new thin film materials, and (IV) Reviews.

I DEVELOPMENT OF NEW TECHNIQUES FOR THE STUDY OF HYDROGEN IN MATERIALS

When we started this project, most of our work in the use of MeV ion beams for the study of hydrogen in materials had been applied to the study of insulators and semiconductors, not metals. In some cases, metals present a unique challenge to this type of analysis. For example, in many hydrogen in metals studies, the levels of hydrogen in the samples can be very small (in the ppm level) below the sensitivity then available by nuclear reaction analysis. We have now pushed the sensitivity down to the 1ppm level for both hydrogen and deuterium (paper 15).

In some cases the hydrogen and be very mobile and hydrogen levels in the sample can change rapidly. To follow such a change, one needs to be able to determine the hydrogen concentration very rapidly and with high statistical precision. This led to our development of He induced recoil techniques in a transmission geometry (paper 19) explicitly to study such hydrogen in metals problems and later to the realization that the recoil method had such a high cross-section that one could even make measurements using radioactive alpha-particle sources (paper 17).

Productive study of some hydrogen related materials problems requires that one can measure not only the amount of hydrogen in a sample but also where in the sample it is concentrated. The usual 15N nuclear reaction analysis method is very powerful in that it automatically gives high

depth resolution allowing the measurement of concentration profiles in two dimensional planar samples (e.g. thin films made by electrodeposition, evaporation, CVD,...). However, in cases where one needs to measure hydrogen located on grain boundaries or at crack tips, the usual depth profiling does not give sufficient information. In a attempt to satisfy the demands of such problems, we have developed a prompt radiographic technique for the three dimensional analysis of hydrogen in materials (papers 14 and 18). Because this radiographic method is difficult to apply in some cases, we have also worked using the SUNY Albany rastered microbeam (beam diameter of 2 microns) in conjunction with the He induced H recoil technique to measure the distribution of hydrogen around grain boundaries and crack tips (unpublished). This method looks very promising but we have not yet had the time to fully investigate the potential of this method or to apply it to a physically interesting case.

Another property of some metals which makes analysis of hydrogen in them difficult is the fact that hydrogen can enter and leave these metals depending on their environment. For example, some metals will lose their hydrogen just by being placed in a vacuum. To obviate such potential problems, we have just completed construction and testing of a non-vacuum analysis setup which is capable of carrying out the usual 15N hydrogen profiling measurements while the sample is in a gas environment, at present with gas pressures of up to about 10 Torr. This technique makes use of differential pumping apertures to bring the 15N ion beam from the vacuum of the accelerator into the analysis chamber containing gas. A report describing this work is presently being prepared.

A recent re-measurement of the width of the 15N + H nuclear reaction resonance made us realize that the resonance is so narrow that the normal thermal or zero point motion of hydrogen bound to a surface is sufficient to shift the nuclear reaction off resonance. In other words, if we measure the yield of nuclear reactions vs 15N energy on a very thin target, the width of this yield curve will be dominated by this Doppler broadening. A measurement of this Doppler broadening can be used to learn about the bond that holds the hydrogen to the surface. On single crystals, by studying the Doppler broadening as a function of incident angle, one can study the angular dependence of the bond. These are unique possibilities unavailable by any other known technique. It is too early to know how useful such measurements may turn out to be but it is possible that these observations may lead to the development of a whole new field of surface Doppler spectroscopy. These are difficult experiments requiring careful surface preparation (UHV...) and control over the energy spread in the incident beam. We now believe that we have control over this

experiment and hope to take a definitive set of data over the next few weeks which will then be promptly published.

Finally, our work over the past year or so on the analysis of thin (1 micron) films composed of many layers of component very thin films (of order 100 Angstroms) has led us to the realization that these multilayer materials have great potential both in the engineering of new thin film coatings (by varying the composition and thicknesses of the component layers) and as a tool for the study of the composition, bonding, defects,... of solid-solid interfaces and sub 100 Angstroms films. The basic ideas for the use of these multilayer films is presented in paper (5). An important point to keep in mind when considering technological application of these multilayer materials is that by simply using microprocessor control over the deposition apparatus (e. g. plasma CVD), it is essentially as easy to deposit these designed multilayer thin films as it has been to deposit single component films in the past.

II STUDIES OF MACROSCOPIC VARIABLES ON THE DISTRIBUTION OF HYDROGEN IN METALS

The ability for the first time to quantitatively measure the hydrogen concentration and distribution in metal samples allows for the rather direct test of "conventional" models which predict such basic properties as how hydrogen re-distributes as a result of applied stress, presences of electric currents, or temperature gradients. The basic idea was to first conduct experiments to test the conventional predictions of, for example, the effect of stress in simple systems (e.g. single phase hydrogen in solution). If the experiment and theory agreed in this simple case, that would be evidence both that the theory was correct and that our experimental procedures were reliable. After this, one could then study more complicated cases (mixed phases, hydrides,...) where now the new experimental method could be used to deduce the mobility of hydrogen in these more complicated cases.

During the period of this contract we completed studies of the redistribution of hydrogen as a result of stress (paper 19) and as a result of electric currents (paper 11). These measurements were made in relatively simple systems. We have also recorded data in the stress case for more complicated systems (hydride forming metals) which show interesting but complicated behavior. However, before such data can be meaningfully described in a publication, it will be necessary to carry out measurements on samples which have have been fully characterized by traditional metallographic techniques.

III EFFECTS OF HYDROGEN ON VARIOUS NEW THIN FILM MATERIALS

In addition to the work described above on technique development and application to the motion of hydrogen in metals, we have carried on a large amount of work on the effects of hydrogen in a wide variety of new materials, including electro-deposited Cr (paper 1), ballistically compressed SiO2 (paper 2), zirconium fluoride glass (papers 3 and 20), ion assisted ZrO2 films (paper 4), water in SiO2 (paper 6), adhesion of Au on Si (paper 8), and amorphous carbon films (papers 9 and 13).

The application of nuclear reaction analysis for hydrogen in these many materials is diverse and we will not try to summarize the results here. It is best to look at the individual publications.

IV REVIEWS

Finally, we have been asked to write reviews of various aspects of nuclear reaction analysis for several different publications. Review supported by this contract include papers 7, 10, 12 and 14.

PUBLICATIONS

1. Effects of Chromium Electroplating Solution on Compositionof the Properties of Deposits.
A. M. Kasaaian, J. Dash and W. A. Lanford
Proceedings, 72nd AES Annual Conference, Detroit, July 1985.

2. Effects of Hot Dense Gases on the Structure and Composition of Materials.
J. Dash, M. Takeo, A. R. Trzynka, J. M. Roush, A. M. Kasaaian, F. B. Brace, P. G. Weaver and W. A. Lanford
Proceedings, International Conference on Metallurgical Applications of Shock Wave and High Strain Phenomena, July 28- August 1, 1985, Portland, Oregon.

3. Durable Surfaces on Zirconium Fluoride Glass,
C. Burman and W. A. Lanford
Applied Physics Letters 44 (1984)845.

4. Ion-Assisted Deposition of Bulklike ZrO2
P. J. Martin, R. P. Netterfield, W. G. Sainty, G. J. Clark, W. A. Lanford and S. Sie.
Applied Physics Letters 43 (1984) 711.

5. Use of Superlattices to Determine the Bulk and Interface Stoichiometry of Very Thin Films.
W. A. Lanford and B. Abeles
Nuclear Instruments and Methods (1986) in press.

6. Diffusion of Water in SiO2 at Low Temperature
W. A. Lanford, C. Burman and R. H. Doremus
Proceedings, International Conference on Materials Characterization II, Ed. R. L. Snyder, R. A. Condrate and P. F. Johnson, Plenum Press (1985) 203.

7. Nuclear Reaction Analysis for Diffusion Studies
W. A. Lanford, R. Benenson, C. Burman, and L. Wielunski
Nontraditional Methods in Diffusion, Ed. G. F. Murch, H. K. Birnbaum, and J. R. Cost, Metallurgical Society of AIME, Warrendale, Pa (1984) 155.

8. Ion Beam Enhanced Adhesion of Au Films on Si and SiO2
A. E. Berkowitz, R. E. Benenson, R. L. Fletcher, L. Wielunski, and W. A. Lanford.
Nuclear Instruments and Methods B7/8 (1985) 877.

9. Optical Properties of Hydrogenated Amorphous Carbon Films Made From Methane Plasma.
J. J. Pouch, S. A. Alterovitz, T. D. Warner, D. C. Liu and W. A. Lanford.
Proceedings, Materials Research Society Spring Meeting, April 15-19, 1985, [illegible].

10. Analysis with Heavy Ions
in Heavy Ion Science, Ed. D. A. Bromley, Plenum Press (1985) Volume 6.

11. Direct Concentration Measurement of Hydrogen Electromigration Using Nuclear Reaction Analysis.
R. E. Benenson, P. Berning and L. Wielunski
in Electron Packaging and Materials Science, Ed. E. A. Geiss, K-N Tu and D. R. Uhlman, MRS, Pittsburgh (1985)336.

12. Nuclear Reaction Techniques in Materials Analysis.
G. Amsel and W. A. Lanford
Annual Review of Nuclear and Particle Science 34 (1984) 435.

13. Plasma Deposited Hydrogenated Carbon on GaAs and InP.
J. D. Warner, J. J. Pouch, S. A. Alteroritz, D. C. Liu and W. A. Lanford
Journal of Vacuum Science and Technology A3 (1985)900.

14. 1-D and 3-D Nuclear Reaction Analysis for Hydrogen: Principles and Applications,
W. A. Lanford and C. Burman, Transactions of American Nuclear Society 41 (1982) 473.

15. High Sensitivity Hydrogen Analysis Using Elastic Recoil in UHV.
L. Wielunski, R. Benenson, K. Horn and W. A. Lanford
Nuclear Instrument and Methods (1986) in press.

16. Computer Simulation of He-Induced Forward Recoil Proton Spectra for Hydrogen Concentration Determinations.
R. E. Benenson, L. Wielunski, and W. A. Lanford
Nuclear Instruments and Methods (1986) in press.

17. Use of Alpha Sources of Hydrogen Analysis
W. A. Lanford, L Wielunski and R. Benenson
Journal of Applied Physics 58 (1985) 4.

18. A Technique of the Quantitative Measurement of the Lateral and Depth Distribution of Hydrogen in Solids.
W. A. Lanford and C. Burman
Applied Physics Letters 41 (1982) 2312.

19. He-Induced Hydrogen Recoil Analysis for Metallurgical Applications.
L. Wielunski, R. Benenson and W. A. Lanford
Nuclear Instruments and Methods 218 (1983) 120.

20. Reaction of Zirconium Fluoride Glass with Water: The Kinetics of Dissolution
R. H. Doremus, D. Murphy, N. P. Bansal, W. A. Lanford

and C. Burman
Journal of Material Science 20 (1985) 4445.

SCIENTIFIC PERSONNEL

W. A. Lanford, Principal Investigator

R. Benenson, Principal Investigator

L. Wielunski, Research Associate

K. Horn, Graduate Student - MS granted in 1985 *

P. Berning, Graduate Student - MS granted in 1984 *

J. Hasbun, Graduate Student

J. Roy, Graduate Student

J. Nelson, Undergraduate Student

S. Jones, Undergraduate Student

---

* Both these students have largely finished the experimental work for their PhD degrees while under the support of this contract. They are presently writing their theses.

END

DTIC

7-86